

IV.D.1 A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part I

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Objectives

- Bring together an eclectic group of scientists with experience in materials discovery and theoretical prediction of properties to work on developing new types of hydrogen storage materials.

Particular emphasis is placed on exploring the possibilities of the following types of materials for meeting the 2010 DOE hydrogen storage system targets, especially specific energy, energy density, durability, and uptake and discharge kinetics:

- Nanoporous polymers
- Nanoporous coordination solids
- Destabilized high-density hydrides
- Nanostructured boron nitride
- Magnesium and light alloy nanocrystals

Note that only the research on nanoporous polymers, nanoporous coordination solids, and destabilized high-density hydrides is funded through this

award, with the other subprojects being funded through Basic Energy Sciences.

Technical Barriers

This project addresses the following technical barriers from the On-Board Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Weight and Volume
- (C) Efficiency
- (D) Durability
- (E) Refueling Time
- (M) Hydrogen Capacity and Reversibility
- (N) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The main focus will be on meeting the following specific targets:

- By 2010, develop and verify on-board hydrogen storage materials achieving storage system targets of 2 kWh/kg (6 wt%), 1.5 kWh/L, fill time of 3 min for 5 kg of hydrogen, and \$4/kWh (Table 1).

Accomplishments

- Optimized conditions for the synthesis and activation of $Zn_4O(BDC)_3$ without exposure to atmospheric water, resulting in a Brunauer-Emmett-Teller surface area of 3,800 m²/g.
- Performed high-pressure H₂ adsorption measurements on air-free $Zn_4O(BDC)_3$, revealing record H₂ storage characteristics: 10.5 wt% and 77 g/L at 77 K and 170 bar.
- Performed kinetics measurements on the uptake of H₂ within air-free $Zn_4O(BDC)_3$, revealing a loading time of less than 2 min upon exposure to 45 bar of cold (77 K) H₂.
- Demonstrated 24 cycles of H₂ loading and complete discharge for air-free $Zn_4O(BDC)_3$ without loss of capacity.
- Optimized methods for the attachment of Cr(CO)₃ and Mo(CO)₃ units to the benzene rings within $Zn_4O(BDC)_3$ to generate $Zn_4O[(BDC)Cr(CO)_3]_3$ and $Zn_4O[(BDC)Mo(CO)_3]_3$.

TABLE 1. On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 System Target	FY08 materials*
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	7.1 excess wt% at 77 K and 40 bar for air-free Zn ₄ O(BDC) ₃ (SA 3,800 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	11.5 total wt% at 77 K and 170 bar for air-free Zn ₄ O(BDC) ₃ (SA 3,800 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	2.3 wt% at 298 K and 70 bar for air-free Zn ₄ O(BDC) ₃ (SA 3,800 m ² /g)
Energy Density	kWh/L (g H ₂ /L)	1.5 (45)	77 g H ₂ /L at 77 K and 170 bar for air-free Zn ₄ O(BDC) ₃ (SA 3800 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	3.8 wt% at 77 K and 45 bar for hypercrosslinked polystyrene (SA 1,930 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	1.9 wt% at 77 K and 23 bar for hypercrosslinked polyaniline (SA 630 m ² /g)

*Values given are for the materials alone, not a complete storage system.

- Demonstrated use of photolysis to generate Zn₄O[(BDC)Cr(CO)₂(H₂)₃]₃, which is stable indefinitely at 298 K, indicating a record H₂ binding enthalpy.
- Performed further characterization of hypercrosslinked polystyrene exhibiting a surface area of 1,930 m²/g and an H₂ uptake capacity of 3.8 wt% at 77 K and 45 bar.
- Investigated new methods for synthesizing hypercrosslinked polyaniline. The best sample exhibited reversible H₂ uptake of 1.9 wt% at 77 K and 23 bar, with enhanced H₂ adsorption enthalpies as high as 9.3 kJ/mol.
- Utilized computational methods in examining changes in H₂ binding energies (0.97-4.1 kcal/mol) with variation of the halogen X in the hypothetical clusters [Zn₄X(tetrazolate)₈]¹⁻. The results suggest promising new synthetic targets for metal-organic frameworks.
- Probed the viability of the spill-over mechanism, by using computational methods to determine H₂ binding energies on pyrene. The results indicated at best an energy of 28.7 kcal/mol relative to two H atoms.
- Investigated hydrogen storage in a 9:1 mixture of MgH₂ and MgF₂. This sample desorbed 6.1 wt% of hydrogen at 763 K and 0 bar, then took up 7.4 wt% at 573 K and 45 bar. Again at 763 K and 0 bar, it desorbed 7.4 wt%.



Introduction

Known hydrogen storage materials exhibiting promise include nanostructured carbon-based solids, chemical hydrides, and metal hydrides. Although worthy of significant further investigation, it is by no means clear that any of these systems will be able to meet the DOE performance targets for 2010. We are therefore undertaking a broad-based and coordinated effort to search for new classes of hydrogen storage materials.

Approach

The combined team of UC-Berkeley and LBNL have formed a collaborative, interdisciplinary group to research promising nanostructured materials for hydrogen storage. A total of eight themes or subprojects are currently underway; the following four are funded through this award:

- Synthesis and characterization of nanoporous coordination solids (Long).
- Synthesis and characterization of nanoporous polymers (Fréchet).
- First-principles determination of H₂ binding energies with predictive applications in design of new nanoporous hydrogen storage materials (Head-Gordon).
- Synthesis and characterization of destabilized high-density hydrides (Richardson).

Our approach will be to explore numerous possibilities for new materials, and narrow our focus as the research progresses. The synergy of many scientists in one location working toward a common goal is expected to accelerate our progress and lead to new ideas via cross-fertilization.

Results

Microporous Metal-Organic Frameworks: We have developed an improved synthesis for Zn₄O(1,4-benzenedicarboxylate)₃ that increases maximum uptake from 4.9 excess wt% H₂ to 7.1 excess wt% H₂ at 40 bar. Using our high-pressure sieverts apparatus, we have performed further H₂ adsorption measurements on this material at pressures up to 170 bar. These measurements show that at 170 bar, Zn₄O(1,4-benzenedicarboxylate)₃ adsorbs 11.5 wt% H₂, corresponding to 77 g H₂/L, the highest H₂ uptake capacities yet demonstrated for a cryogenic hydrogen storage material (see Figure 1). Kinetics measurements performed using the same apparatus showed that with an applied pressure of 45 bar, H₂ uptake achieved saturation in ca. 2 min (see Figure 2). Furthermore, the uptake was found to be fully reversible, showing no detectable loss in capacity after 24 adsorption-desorption cycles.

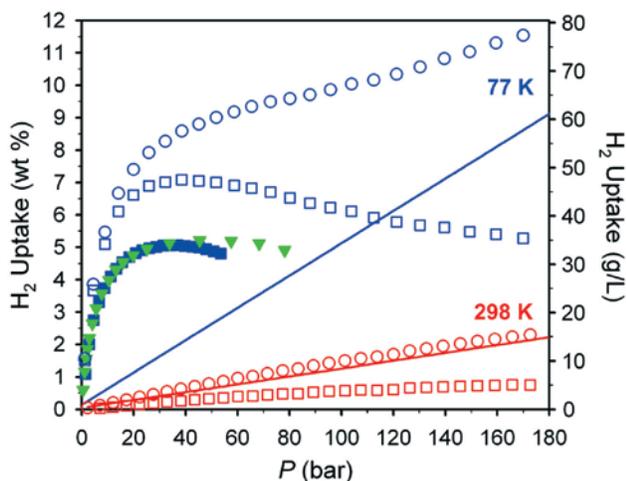


FIGURE 1. Hydrogen adsorption isotherms for samples of $\text{Zn}_4\text{O}(\text{BDC})_3$ prepared with (filled symbols) and without (open symbols) exposure to air, and as reported in previously (green triangles). Data were measured at 77 (blue) and 298 (red) K, and are shown as excess (squares) and total (circles) uptake. All isotherms showed full reversibility without hysteresis. Solid lines indicate the density (righthand scale) of pure H_2 gas.

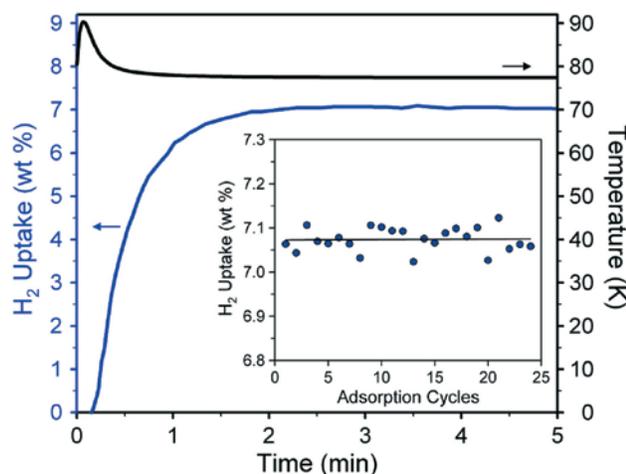


FIGURE 2. Kinetics trace (blue line) for excess H_2 uptake upon exposure of a liquid nitrogen-bathed sample of **1** to a pressure of 45 bar of H_2 gas at 298 K. Note that it takes almost 1 min for the temperature (black line) to return to 77 K. Inset: Excess uptake capacity of **1** measured for sequential H_2 adsorption/desorption cycles.

We have also continued our investigation into porous coordination solids containing low-valent transition metal complexes. Previously, we described the synthesis of $\text{Zn}_4\text{O}[(\text{BDC})\text{Cr}(\text{CO})_3]_3$ ($\text{BDC}^{2-} = 1,4$ -benzenedicarboxylate). Our recent work has focused on finding methods to remove these carbonyl ligands to create coordinatively unsaturated chromium atoms. We have found that photolysis ($\lambda = 450$ nm, full width at half maximum = 70 nm) of $\text{Zn}_4\text{O}[(\text{BDC})\text{Cr}(\text{CO})_3]_3$ under a flow of dinitrogen or dihydrogen generates

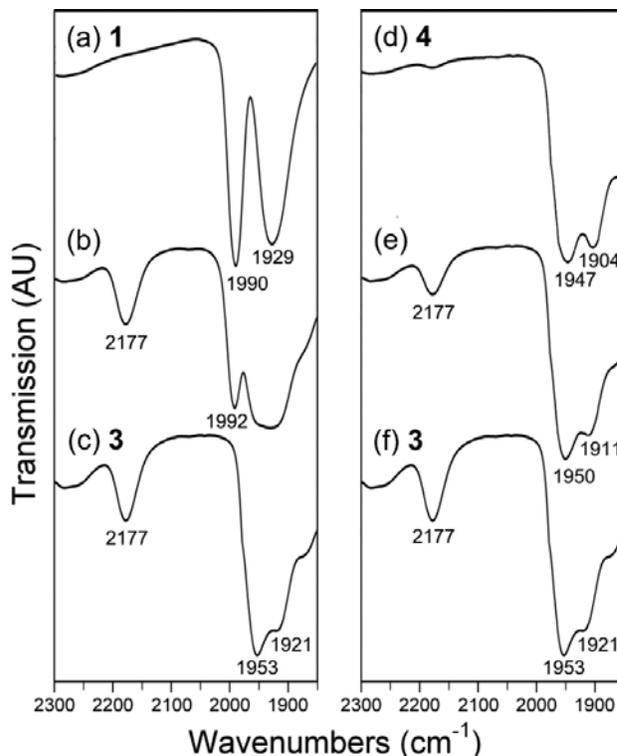


FIGURE 3. (a-c) Infrared spectra of $\text{Zn}_4\text{O}[(\text{BDC})\text{Cr}(\text{CO})_3]_3$ (**1**), after 0 (a), 2 (b), and 5 (c) h of irradiation under a flow of N_2 . (d-f) Infra-red spectra of **1** after 10 h of irradiation under a flow of H_2 to give $\text{Zn}_4\text{O}[(\text{BDC})\text{Cr}(\text{CO})_2(\text{H}_2)]_3$ (**d**), and **4** after exposure to N_2 for 2 (e) and 12 h (f) to give compound **3**.

$\text{Zn}_4\text{O}[(\text{BDC})\text{Cr}(\text{CO})_2(\text{L})]_3$ ($\text{L} = \text{N}_2$ or H_2), as evidenced by the infrared spectra shown in Figure 3. These compounds have been found to be remarkably stable, showing no signs of decomposition after several weeks at room temperature under and N_2 or H_2 atmosphere, respectively. This is a tremendous increase in stability when compared with $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$, which has a $t_{1/2}$ of ca. 3 min at 25°C in supercritical Xe under 62,000 torr of H_2 . Future work with these materials will focus on finding methods for removing additional carbonyl ligands, as well as producing sufficient quantities of the decarbonylated material to study its gas adsorption properties.

Discrete coordination complexes have been reported for all first-row transition metal ions in which a dimetallic center is bridged by four carboxylate groups in a paddlewheel geometry. We postulated therefore that it should be feasible to synthesize isostructural metal-organic frameworks where the metal ions differ. To determine which metal ion affords maximal hydrogen adsorption enthalpy, we have accomplished the syntheses of $\text{Zn}_3(\text{BTC})_2$, $\text{Cu}_3(\text{BTC})_2$, $\text{Cr}_3(\text{BTC})_2$ and $\text{Mo}_3(\text{BTC})_2$ ($\text{BTC}^{3-} = \text{benzene-1,3,5-tricarboxylate}$) and are pursuing the analogous frameworks containing Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and W^{2+} . Syntheses for

$\text{Mo}_3(\text{BTC})_2$, $\text{Zn}_3(\text{BTC})_2$, and $\text{Cu}_3(\text{BTC})_2$ have been reported previously, and $\text{Cr}_3(\text{BTC})_2$ was synthesized in a manner analogous to the molybdenum-containing framework. The powder X-ray diffraction patterns of these materials are comparable to that reported for the $\text{Cu}_3(\text{BTC})_2$ framework, confirming these compounds are isostructural. The zero-coverage enthalpy of adsorption of hydrogen to the Cr- and Mo-containing frameworks are 7.4 and 6.1 kJ/mol respectively, as compared to the reported value of 6.8 kJ/mol for the Cu analogue.

We have also recently generated what may be the first lithium-based microporous metal-organic framework, wherein each cluster contains four lithium ions bound to the oxygen atoms of carboxylate groups from tetra(4-carboxyphenyl) adamantane. The incorporation of light-weight metal ions provides an attractive solution to reduce the gravimetric adsorption of hydrogen by these systems. Removal of solvent molecules coordinated to the Li^+ ions could increase the enthalpy of adsorption through direct metal-hydrogen interactions.

Microporous Polymers: Additional H_2 adsorption experiments have been performed on our hypercrosslinked polystyrenes. These materials are based on a nonporous gel-type precursor, and exhibit a specific surface area of 1,930 m^2/g and H_2 storage capacities of 1.55, 3.2, and 3.8 wt% at 77 K and pressures of 1.2, 20, and 45 bar, respectively. Using additional adsorption isotherms collected at 87 K and the van't Hoff equation, we have also determined the initial enthalpy of H_2 adsorption to be 6.6 kJ/mol. Based on the application of density functional theory analysis to a nitrogen adsorption isotherm, the hypercrosslinked polystyrene has a mean pore size of 1.8 nm.

In the past year we have focused our efforts more closely on hypercrosslinked polyanilines synthesized from linear polyaniline via N-alkylation with paraformaldehyde. One of the resulting materials exhibits an enthalpy of H_2 adsorption of up to 9.3 kJ/mol. This brings us closer to hypercrosslinked polymers that can store hydrogen at or near room temperature. Our search for nanoporous materials with enhanced properties enabling hydrogen storage at temperatures higher than 77 K has thus focused on new chemistries. For example, we have developed a method for the preparation of entirely new type of nanoporous materials, hypercrosslinked polyanilines, with permanent porous structure and specific surface areas reaching so far up to 630 m^2/g . The hypercrosslinking reaction was carried out with commercial polyanilines and formaldehyde or diiodoalkanes using both conventional and microwave assisted processes. Polyaniline swollen in an organic solvent was hypercrosslinked to form a rigid, mesh-like polymer with permanent porosity and a high surface area. The resulting materials have been characterized using infrared spectroscopy and elemental analysis. Physical properties were determined

by means of scanning electron microscopy and nitrogen adsorption experiments. We demonstrated that short crosslinks such as those created using formaldehyde and diiodomethane produce materials with the highest surface areas. Surface area also increases with the concentration of polyaniline in solution used during synthesis. The hydrogen storage properties of all materials have been tested. A capacity of 1.9 wt% at 77 K and 23 bar was found for the best sorbent. Further optimization of reaction conditions is expected to lead to materials with much higher surface area and therefore enhanced hydrogen storage capacity. More importantly, hypercrosslinked polyanilines exhibit remarkably high affinity for hydrogen, which results in enthalpies of adsorption as high as 9.3 kJ/mol, a sharp contrast with hypercrosslinked polystyrenes we demonstrated previously, and metal-organic frameworks for which enthalpies of adsorption typically in a range of 4-7 kJ/mol.

Earlier, we synthesized hypercrosslinked polyanilines from linear polyaniline with diiodomethane as the crosslinker. We have tested several other diiodoalkanes and determined that the surface area and hydrogen storage capacity of the resulting materials is likely a function of the rigidity of the crosslinks involved. We have also established relationships between surface area and synthesis conditions. Knowledge of these relationships may allow us to produce hypercrosslinked polyanilines with surface areas higher than the 630 m^2/g that we have synthesized thus far.

Recent publications have demonstrated substantial hydrogen storage ability of porous materials at room temperature based on a phenomenon called spillover. In this process, H_2 dissociates on a metal catalyst and can be transported and stored as H atoms on an adjacent surface. We have therefore initiated experiments directed toward application of the spillover mechanism. We are using our hypercrosslinked polymers with large surface areas for attachment of palladium nanoparticles. Early results indicate that up to three times higher hydrogen storage capacity can be achieved with these materials at room temperature. As a preliminary step to applying spillover to our materials, we have successfully repeated some of the spillover results of Yang, et al. using a carbon support.

We plan now to use our new knowledge of synthesis conditions to produce hypercrosslinked polyanilines with higher surface areas. We are also developing a methodology for generalizing the process of hypercrosslinking to a wide variety of materials such as polypyrrols. Our experiments with spillover will also continue.

Computational Studies of H_2 Binding: Our study on the interaction of molecular hydrogen with open transition metal centers has showed that decorating the organic spacers of metal-organic frameworks

with transition metal centers could create sites with much greater binding affinity than the organic spacer itself. In fact, the binding energies are somewhat too strong to be in the optimal range (we calculate values between 12 and 21 kcal/mol, compared with a desired range of roughly 5-10 kcal/mol). We also investigated the tunability of the binding energy as a function of ligand substitutions on the central organic molecule, as well as a function of other ligands attached to the metal center. We found that fine tuning was possible by remote substitutions. The most promising avenue for future work here is by using the lightest transition metals, which appear likely to have binding energies in the desired range.

Exploration of hydrogen binding to tetrameric Zn centers in metal-organic frameworks. Motivated by experimental activity in the Long group, we have performed preliminary calculations on the structural center shown in Figure 4 – both for the stoichiometry shown and also when Cl is replaced by either lighter or heavier halogens. The results (obtained with a new density functional, wB97X-D, we have developed that correctly incorporates dispersion effects) are enumerated in the legend of Figure 4. It is evident that the coordination strength to Zn^{2+} depends quite strongly on the halogen, and approaches (but does not quite reach) the desired energy range.

Exploration of hydrogen addition to graphitic materials as preliminary tests of the viability of storage by a spillover mechanism. Using small polyaromatic

hydrocarbon systems as finite models for graphite, we have explored the energy change for addition of hydrogen (see Figure 5). The results suggest that the overall energy change for this process is not consistent with a material that can store hydrogen with a binding energy in the desired range. It is possible that there are significant size effects to the binding energies (for instance it is striking that the binding per hydrogen atom doubles when two H atoms are added). However, we have not yet further explored these effects, since there are indications that other groups (Jakobsen, Rice) are actively pursuing such calculations.

Destabilized Metal Hydrides: Two fluoride-substituted metal hydride samples were prepared and tested. The first consisted of a mixture of Mg and MnF_2 in a mole ratio of 3:1. The objective was to produce finely divided Mn and MgF_2 by metathesis. The sample absorbed only 1.08 wt% hydrogen at 525 K and 70 bar and desorbed less than 0.1% at 473 K. After desorption, X-ray diffraction showed the presence of MgF_2 , MnH, and Mg. Although the metathesis reaction appears to proceed, complex hydride formation was not enhanced.

The second sample was a mixture of commercial MgH_2 (nominally 90% pure with most of the remainder Mg) and 10 mol% MgF_2 , ball-milled for 20 minutes for mixing purposes only. This sample desorbed 6.1 wt% of hydrogen at 763 K and 0 bar, then took up 7.4 wt% at 573 K and 45 bar. Again at 763 K and 0 bar, it desorbed 7.4 wt%. While the kinetics were not remarkable, the high utilization compares favorably with that found for

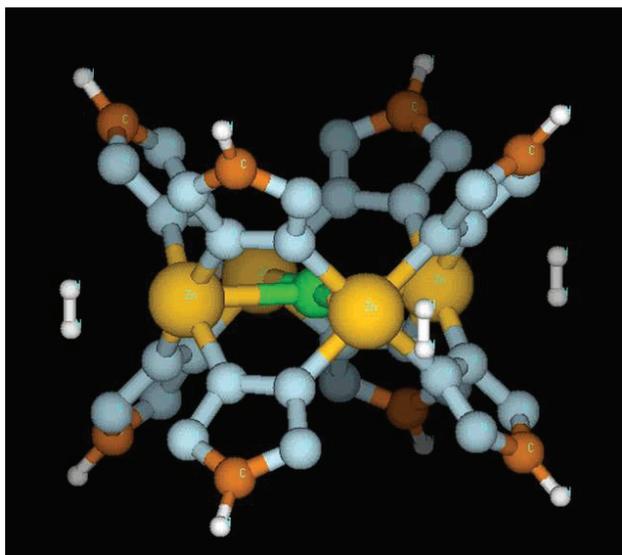


FIGURE 4. Hydrogen binding at exposed Zn^{2+} sites of a hypothetical $[Zn_4X(tetrazolate)_8]^{1-}$ cluster with the square planar structure observed in Mn^{2+} -based metal-organic frameworks exhibiting high H_2 loading at room temperature. The calculated binding enthalpies were found to vary substantially with changes in the central halide anion: 0.97 kcal/mol for $X = F$, 2.4 kcal/mol for $X = Cl$, 3.9 kcal/mol for $X = Br$, and 4.1 kcal/mol for $X = I$.

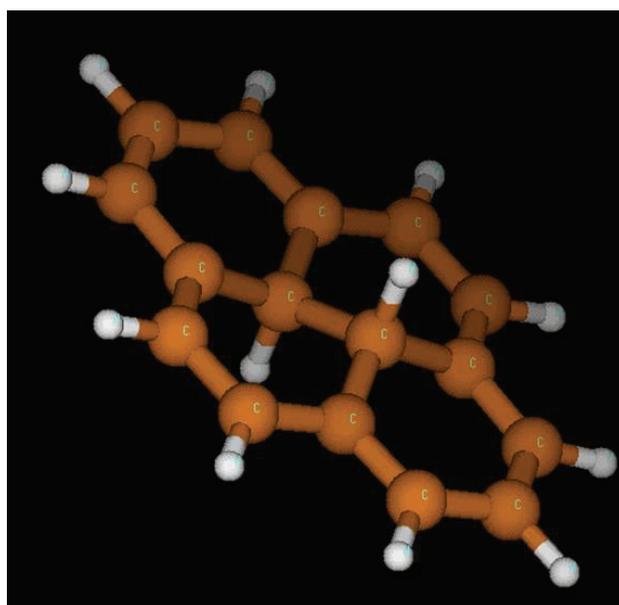


FIGURE 5. Hydrogen binding to pyrene, $C_{16}H_{10}$. Relative to H atoms, the calculated binding energies are 15.2 kcal/mol upon binding one H atom, and 28.7 kcal/mol upon binding two H atoms in a *cis* geometry, and 33.2 kcal/mol upon binding two H atoms in a *trans* geometry (shown).

MgH₂ without added fluoride. Post-testing powder X-ray diffraction measurements showed that fluoride was not lost and the MgF₂ was somewhat more crystalline than before the test. Further testing of this system, including high energy ball milling of the mixture, is in progress.

Conclusions and Future Directions

Synthetic approaches have now been developed for incorporating high concentrations of metal carbonyl units within nanoporous coordination solids and polymers. Methods for displacing CO are now under investigation, and will be followed by H₂ storage measurements for these unique materials. In addition, electronic structure calculations are underway to assess the best combinations of metal center and ligand substituents to adjust the H₂ binding energy.

FY 2008 Publications

1. “Unravelling the Origin of Intermolecular Interactions Using Absolutely Localized Molecular Orbitals” Khaliullin, R.Z.; Cobar, E.A.; Lochan, R.C.; Bell, A.T.; Head-Gordon, M. *J. Phys. Chem. A* **2007**, *111*, 8753-8756.
2. “Localized Orbital Theory and Ammonia Triborane” Subotnik, J. E.; Sodt, A.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5522-5530.
3. “Hydrogen Adsorption in Dehydrated Variants of the Cyano-Bridged Framework Compounds A₂Zn₃[Fe(CN)₆]₂·xH₂O (A = H, Li, Na, K, Rb)” Kaye, S.S.; Long, J. R. *Chem. Commun.* **2007**, 4486-4488.
4. “Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn₄O(1,4-benzenedicarboxylate)₃ (MOF-5)” Kaye, S.S.; Dailly, A.; Yaghi, O.M.; Long, J.R. *J. Am. Chem. Soc.* **2007**, *129*, 14176-14177.
5. “Matrix Isolation Chemistry in a Porous Metal-Organic Framework: Photochemical Substitutions of N₂ and H₂ in Zn₄O[(η⁶-1,4-benzenedicarboxylate)Cr(CO)₃]₃” Kaye, S.S.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 806-807.
6. Interaction of Molecular Hydrogen with Open Transition Metal Centers for Enhanced Binding in Metal-Organic Frameworks: A Computational Study “Lochan, R.C.; Khaliullin, R.Z.; Head-Gordon, M. *Inorg. Chem.* **2008**, *47*, 4032-4044.
7. “Hydrogen Storage in Microporous Metal-Organic Frameworks with Exposed Metal Sites” Dinca, M.; Long, J.R. *Angew. Chem., Int Ed.* **2008**, *47*, in press.

FY 2008 Presentations

- 1–19. “Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites” Long, J. R.: Neutron School, Los Alamos National Laboratory (July 14, 2007); SPIE International Symposium on Optics and Photonics, San Diego, CA (August 28, 2007); University of Nebraska-Lincoln (September 7, 2007); Materials Science & Technology 2007 Conference, Detroit, MI (September 19, 2007); University of Erlangen-Nuremberg (October 5, 2007); Workshop on Metal Rich Compounds, Karlsruhe, Germany (October 9, 2007); University Lectureship, University of Ottawa (October 19, 2007); Argonne National Laboratory (November 1, 2007); University of Delaware (November 14, 2007); UCSB-MPG Workshop on Inorganic Materials for Energy Conversion, Storage, and Conservation, Lake Arrowhead, CA (February 20, 2008); University of Florida (February 25, 2008); University of South Florida (February 28, 2008); Florida State University (February 29, 2008); Caribbean Coordination Chemistry Conference, Cancun, Mexico (March 7, 2008); Simon Fraser University (March 27, 2008); The 235th Meeting of the American Chemical Society, New Orleans, LA (April 7, 2008); American Conference on Neutron Scattering, Santa Fe, NM (May 13, 2008); 8th International Symposium on the Characterization of Porous Solids, Edinburgh, Scotland (June 12, 2008); Université Louis Pasteur, Strasbourg, France (June 19, 2008).